2021 DOE Vehicle Technologies Office
Annual Merit Review

Diesel-like fuels, combustion, and emissions

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Project ID # ft093

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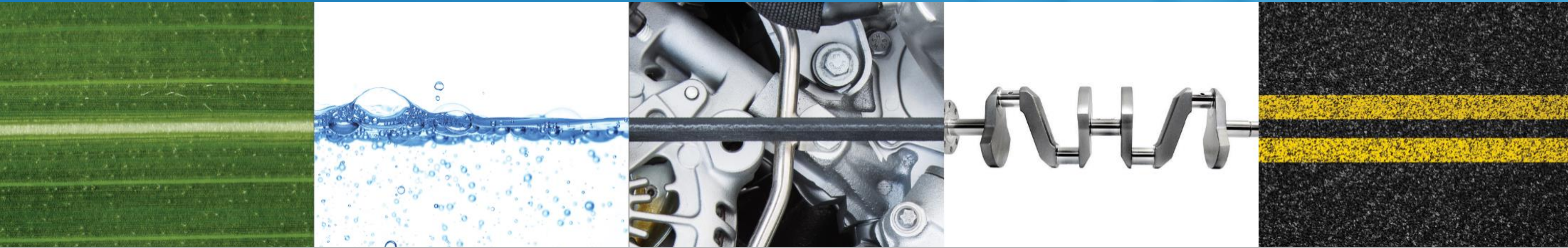
CO-OPTIMIZATION OF
FUELS & ENGINES

better fuels | better vehicles | sooner



Relevance of low-carbon fuels in medium/heavy-duty vehicles

- **Displacing fossil-derived diesel fuel with low-carbon, bio-based alternatives reduces the GHG emissions of medium- and heavy-duty vehicles**
  - *Rapid deployment:* utilize existing infrastructure for production, transport, and distribution
  - *Unique impact:* decrease carbon footprint of vehicles already on the road and in applications where battery-electric vehicles aren't viable

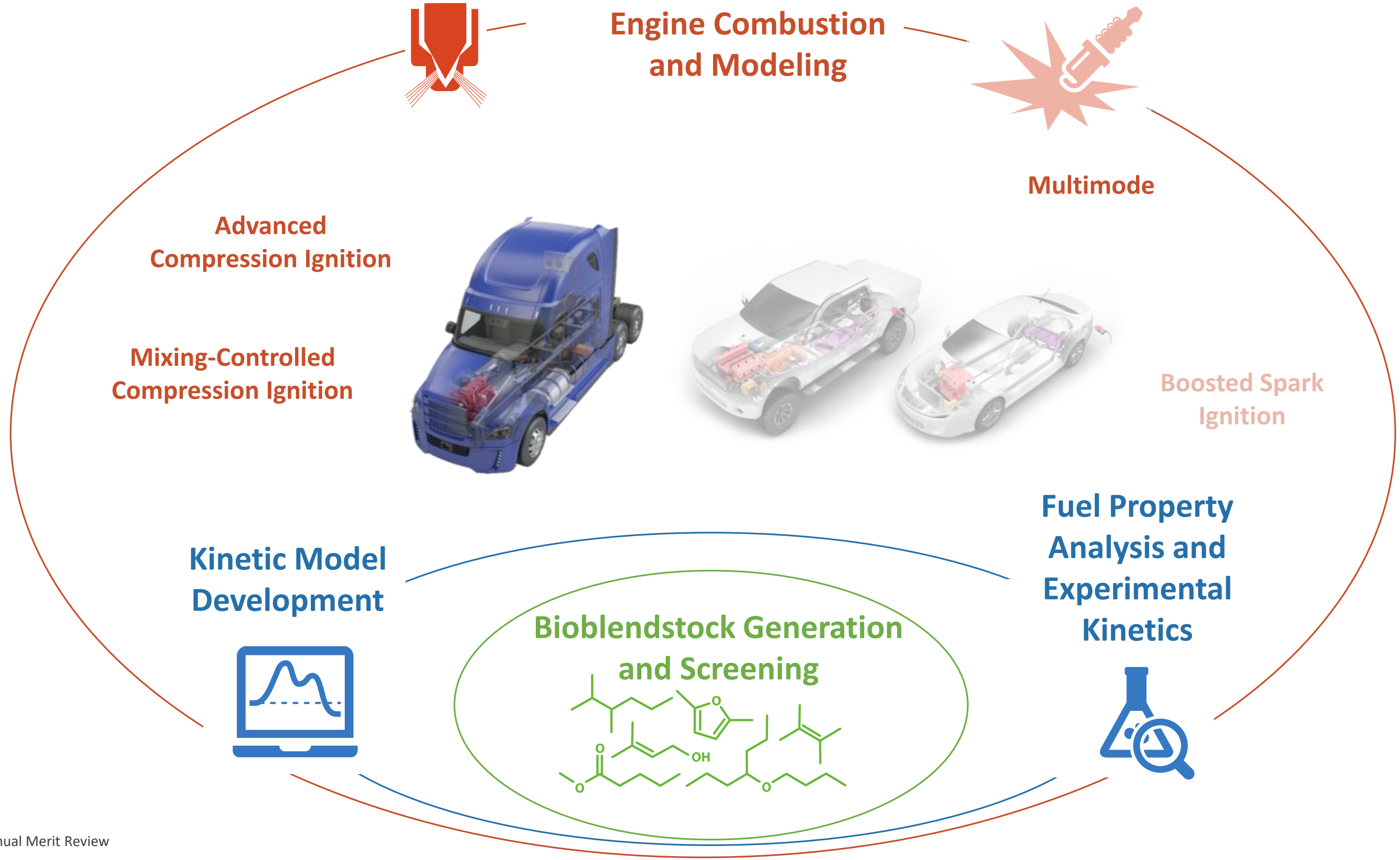
- **Low-carbon bio-blendstocks can reduce GHG emissions by over 60% compared to fossil diesel and add value for refiners**

- **Introducing new fuels to the market is extremely challenging; requires comprehensive understanding of how fuels impact:**
  - Life-cycle GHG emissions
  - Refinery optimization and economics
  - Infrastructure
  - Combustion in present and future engines
  - Aftertreatment systems and emissions regulations

Outline

- **Co-Optima teams**
- **Identification and evaluation of diesel-like bio-blendstocks**
  - Tiered screening approach
  - Economic and environmental benefits
  - Top bio-blendstock candidates
  - Addressing barriers to adoption
- **Effects on combustion and emissions performance**
  - MCCI combustion including catalyst heating operation
  - Ducted fuel injection
  - Chemical kinetics
  - ACI/multimode and exhaust aftertreatment
- **Ongoing work, remaining challenges, and summary**

Collaborative Effort from all Co-Optima Teams

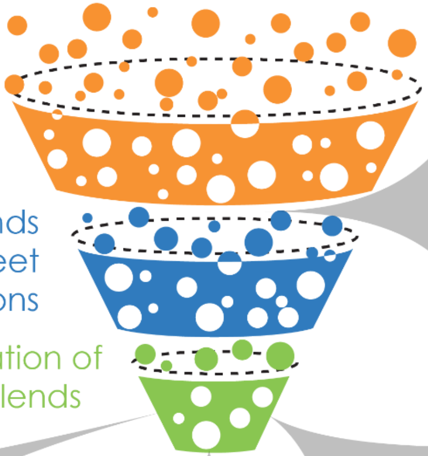


Tiered Screening Approach for Diesel Blendstocks

Tier 1: Identify attractive blendstocks using computational methods and measurements on small quantities

Tier 2: Determine if blends with fossil diesel can meet ASTM specifications

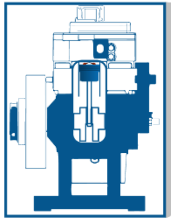
Tier 3: Evaluation of candidate blends



Tier 1 merit table

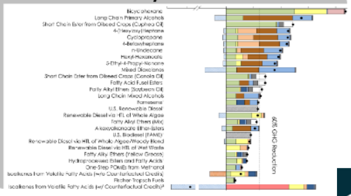
MCCI Bio-Blendstocks	LHV (MJ/kg)	Cetane	Melting Pt (°C)	Flash Pt (°C)	Water Sol (g/L)	YSI
Biodiesel (mixture)	37.5	47	-20	>130	<1	-
Renewable Diesel (mixture)	42 to 44	>70	-25	>68	<0.1	-
Farnesane	43.3	58.6	-73	110	<0.1	110
HTL Bio-Oil, sewage sludge (mixture)	>40	>60	5	55	-	-
EtOH-to-Isoalkanes (mixture)	43.8	55 to 68	-60	>54	<0.1	-
4-Butoxyheptane	39	80	<-80	64	<0.1	58
5-Ethyl-4-Propylnonane	44	48	<-80	74	<0.1	110
HTL Bio-Oil, wood/algae (mixture)	>40	40	-	-	-	-
POMEs (series)	19 to 30	73 to 79	<0	62 to 63	0.8 to 250	2-37
Dioxolanes (series)	28 to 34	32 to 91	<0	33 to 78	<0.1 to 8000	48 to 69
Alkoxyalkanoate Esther-Ether (series)	32 to 34	42 to 62	<-10	-	-	22 to 90
Fatty alkyl ethers (series)	41 to 42	97 to 104	-11 to -16	-	<1	196 to 198
Hexyl hexanoate	35	40	-55	99	<0.1	61
Methyl decanoate	34	52	-18	111	<0.1	50
Fatty acid fusel esters (mixture)	>37	>70	>10	-	-	-
Derivatives of Myrcene (series)	43 to 43	43 to 58	<-40	88 to 158	<0.1	131 to 187
Di-Cyclohexanes/cyclopentanes	40.7	40.9	<0	92	<0.1	110
n-Undecane	44.2	71	<-26	65	<0.1	65
Cyclopropanes (series)	>40	>40	<-10	-	<0.1	122 to 142
Oxetanes (series)	37 to 39	55 to 63	<-20	-	-	52 to 90
Branched long chain R-OHs (catalysis mixture)	>40	22 to 39	<-10	-	<0.1 to 30	83 to 107
Branched long chain R-OHs (bio series)	>40	>40	-19 to -41	>100	<0.1	84 to 95
2-Nonanol	38	40	-36	96	0.46	52
Dipentyl ether	39	111	-69	57	35	44
Butylal	33.8	70	-58	62	0.3	48

Effects on engine performance, combustion, and emissions



Refinery blending analysis

TEA/LCA

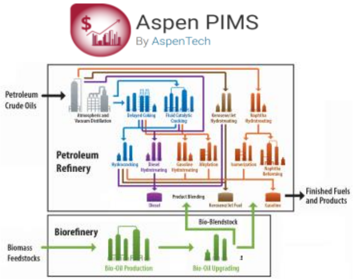


Refinery and life-cycle analyses demonstrate bio-blends can add value for refineries and provide GHG reductions

Approach: identify fuel properties that would generate market pull from refiners; quantify economic and environmental benefits of bio-blends that meet fuel specifications

- Refinery config. / unit capacity
- Bio-blendstock blending properties
- Standards for fuel blend specifications
- Crude and product pricing data
- Fuel market projections

Optimizable Refinery Models

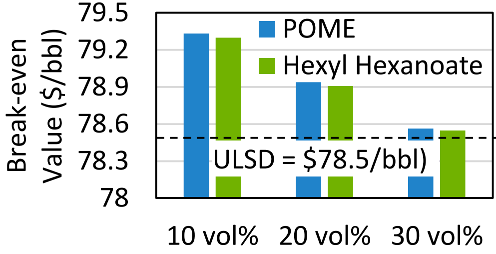


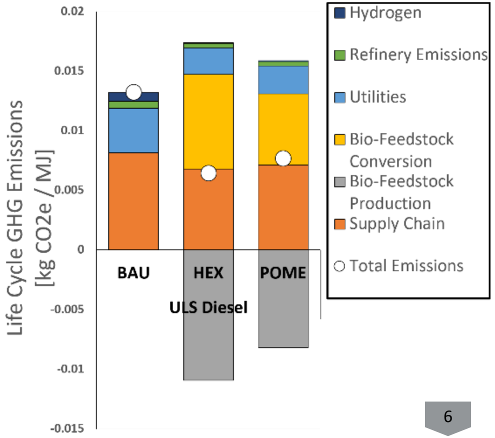
Life Cycle Analysis

Result: Low-sulfur bio-blendstocks add value and break-even values are often greater than ULSD

Result: quantification of reduction in life-cycle GHG emissions of refinery streams

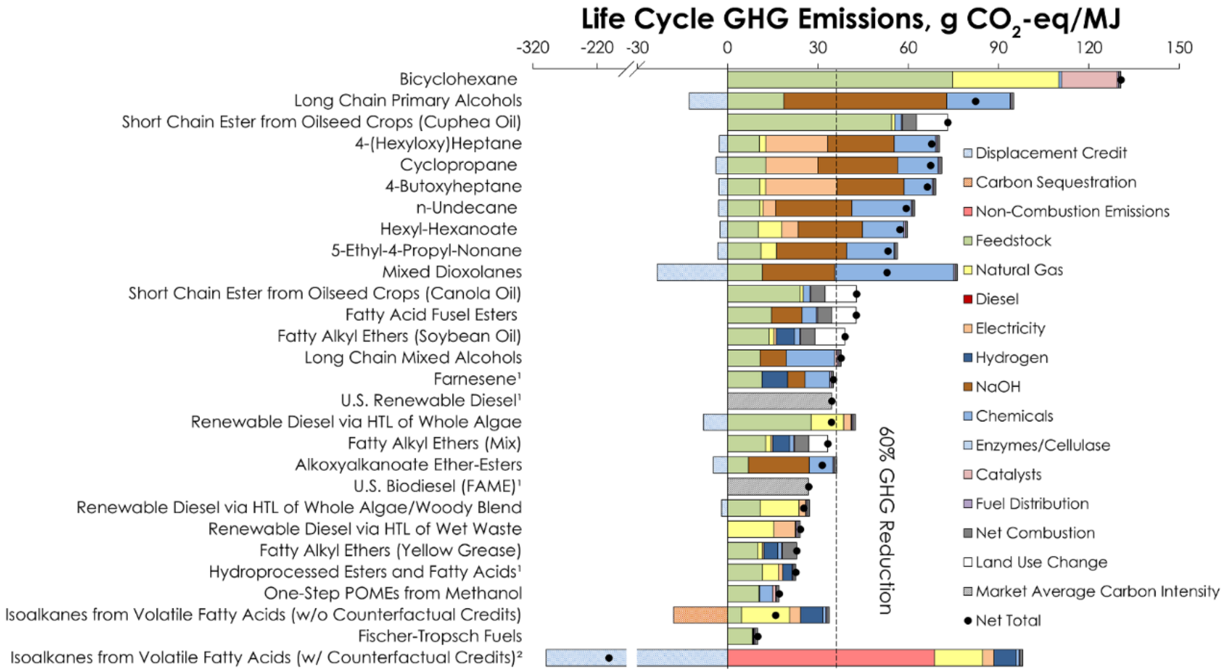
Samples of typical results





Multiple bio-blendstocks achieve 60%+ reductions in GHG compared to fossil diesel

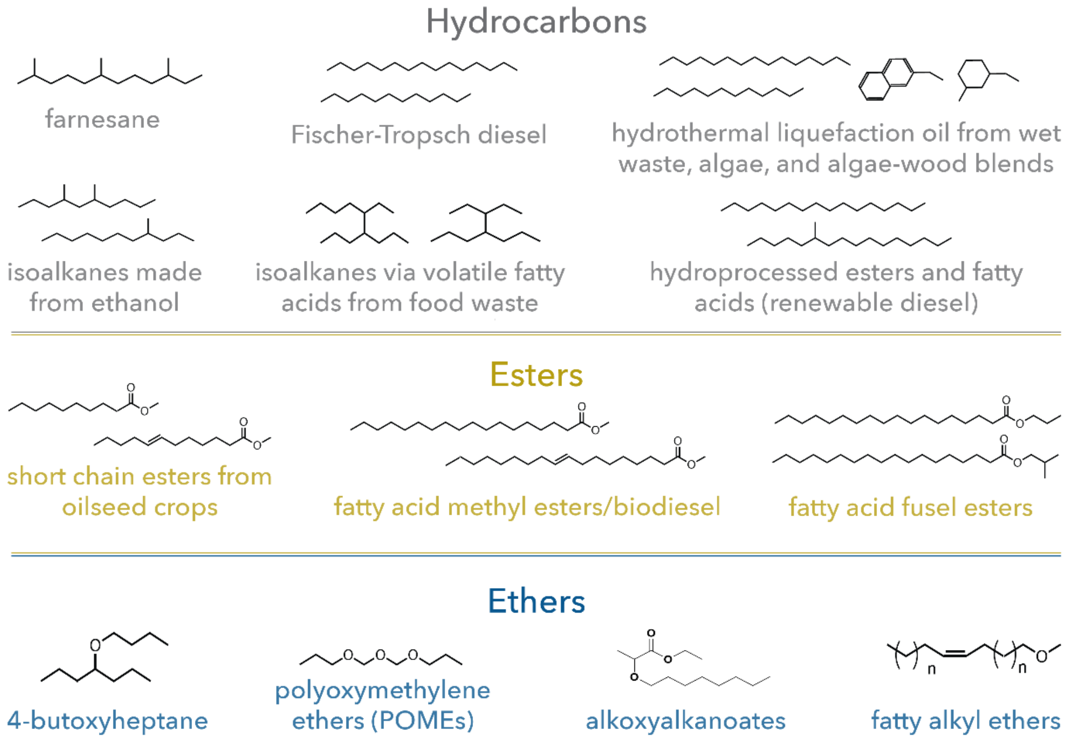
- **Approach:** life cycle analyses of each bio-blendstock
- **Result:** many candidates have been identified that meet or exceed EPA requirements for renewable cellulosic biofuels
  - Life-cycle GHG emissions reduced by 60% or more compared to fossil diesel
- **Significant reductions in GHG emissions are possible through multiple pathways**



[1] *GHG emissions of these pathways are from either an earlier study or average of market fuels.*
[2] *The negative GHG emissions from the "Isoalkanes from Volatile Fatty Acids" pathway is because of the credits of avoided emissions from landfill of the food waste feedstock.*

Thirteen diesel-like blendstocks identified with potential to reduce GHG by 60%+ with reduced criteria emissions

- **GHG emissions of blendstock reduced by 60%+ compared to fossil diesel**
- **CN > 40 (most > 48), LHV > 28 MJ/kg, acceptable flashpoint and cloud point**
  - Additives required to meet some properties
- **Potential to be economically produced at larger scales in most cases**
- **Potential to reduce criteria emissions relative to market diesel**

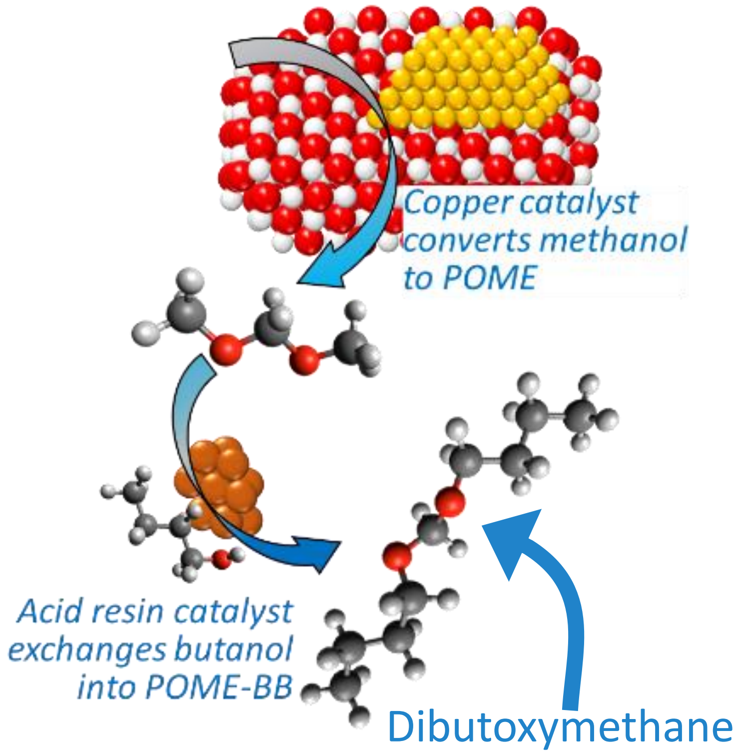


POME-BB: a promising bio-blendstock with a commercially available surrogate

- NREL's innovative approaches have identified the end-exchanged POME-BB mixture and a means to produce it from low net-carbon precursors
  - POME-BB removes two key barriers with POMEs while maintaining high cetane rating and low yield sooting index

	POME	POME-BB
Water solubility	0.6-258 g/L	< 2 g/L
LHV	19 MJ/kg	30 MJ/kg
DCN	>70	
YSI	<50	

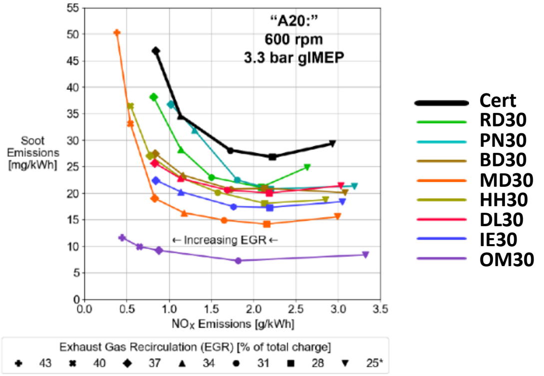
- Scaled-up production processes are in development
- Dibutoxymethane (DBM) is commercially available and makes up a significant fraction of the POME-BB mixture
  - DBM has been selected for various engine experiments



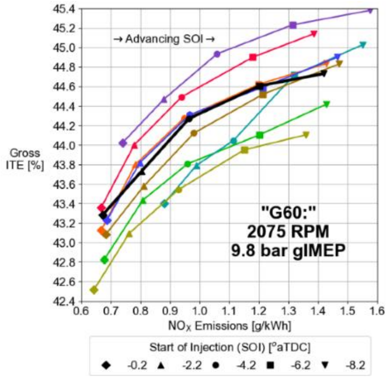
Bio-blendstocks improve the soot-NOx tradeoff with MCCI operation

- **Approach:** quantify emissions and efficiency benefits of a eight different bio-blends for MCCI operation
  - 30% blending into fossil diesel
- **Results:**
  - Oxygenated bio-blends effectively reduce soot emissions, and can extend EGR tolerance over certification ULSD
  - The POME bio-blend most effectively reduces soot and improves efficiency for a fixed injection timing and for a fixed NOx emissions level
- **Oxygenated fuels combined with optimized calibrations may enable further efficiency improvements**

Significant improvements in soot emissions and extended EGR tolerance for bio-blends

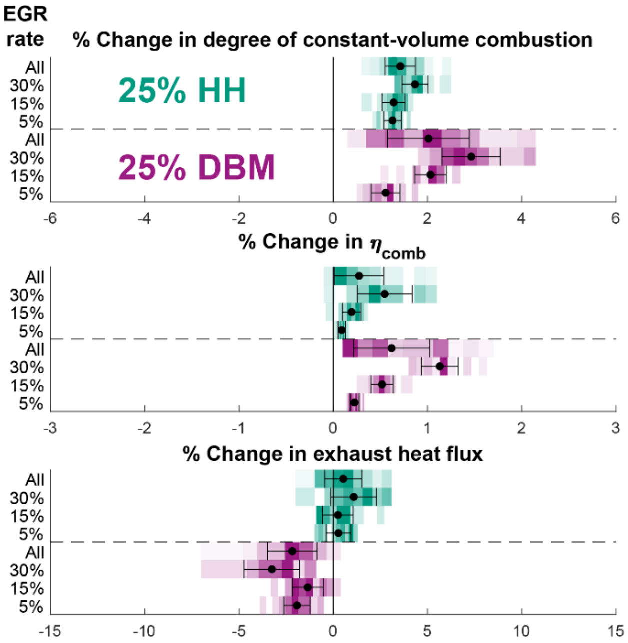


POME blend shows thermal efficiency improvements



Oxygenated bioblends promote clean, efficient combustion but catalyst heating operation may require calibration adjustments

- **Approach:** single-cylinder engine experiments; statistical experiment design to study wide range of catalyst heating operation with 5-injection strategy
- **Results:**
  - For a given calibration, oxygenates typically:
    - Burn faster than fossil diesel fuel
    - Produce fewer emissions than fossil diesel
  - Engine calibrations may need to be adjusted to maintain catalyst heating performance with oxygenated, more reactive bio-blendstocks
- **Multiple fuel properties influence catalyst heating operation; biofuels may necessitate different operating parameters for optimal performance**



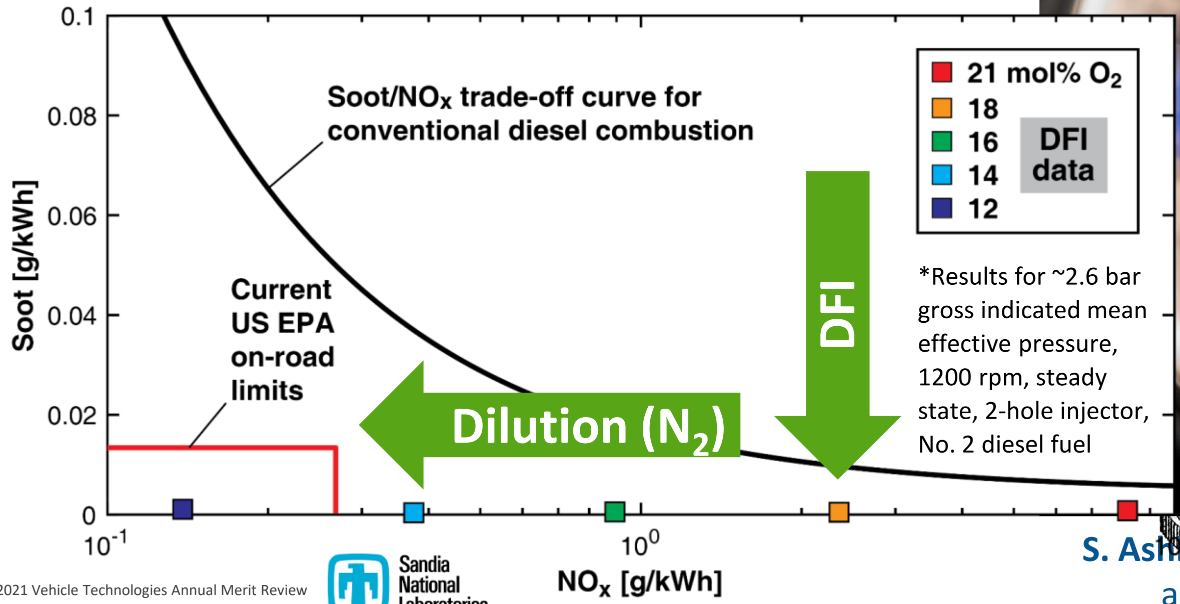
Faster combustion

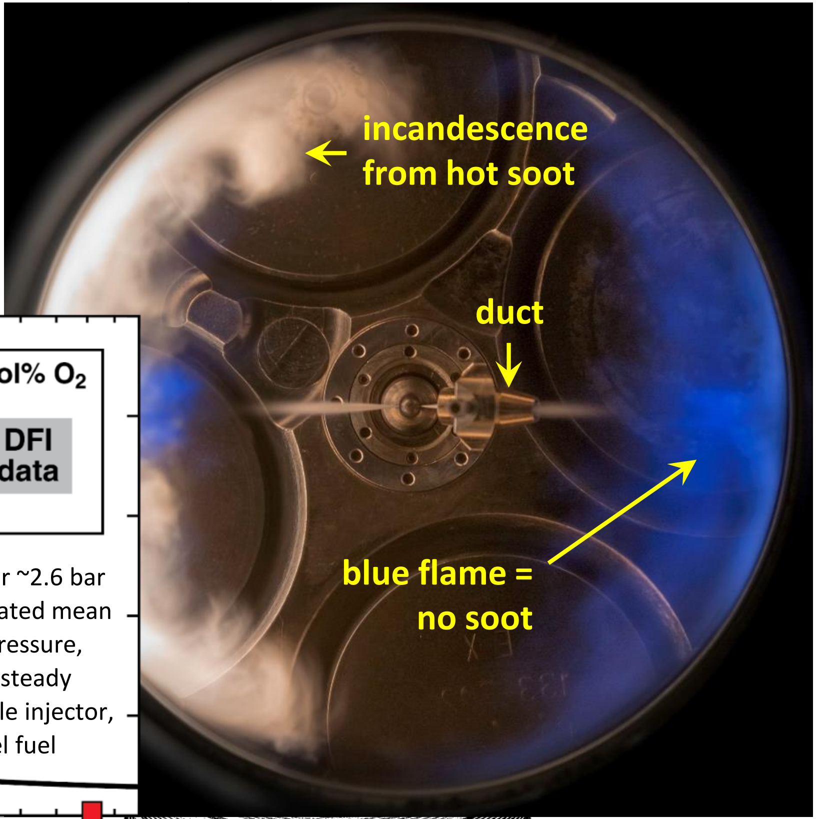
Fewer emissions

Calibration adjustments may be required

Co-Optima funding enabled the first engine and fuel-effects testing of ducted fuel injection (DFI).

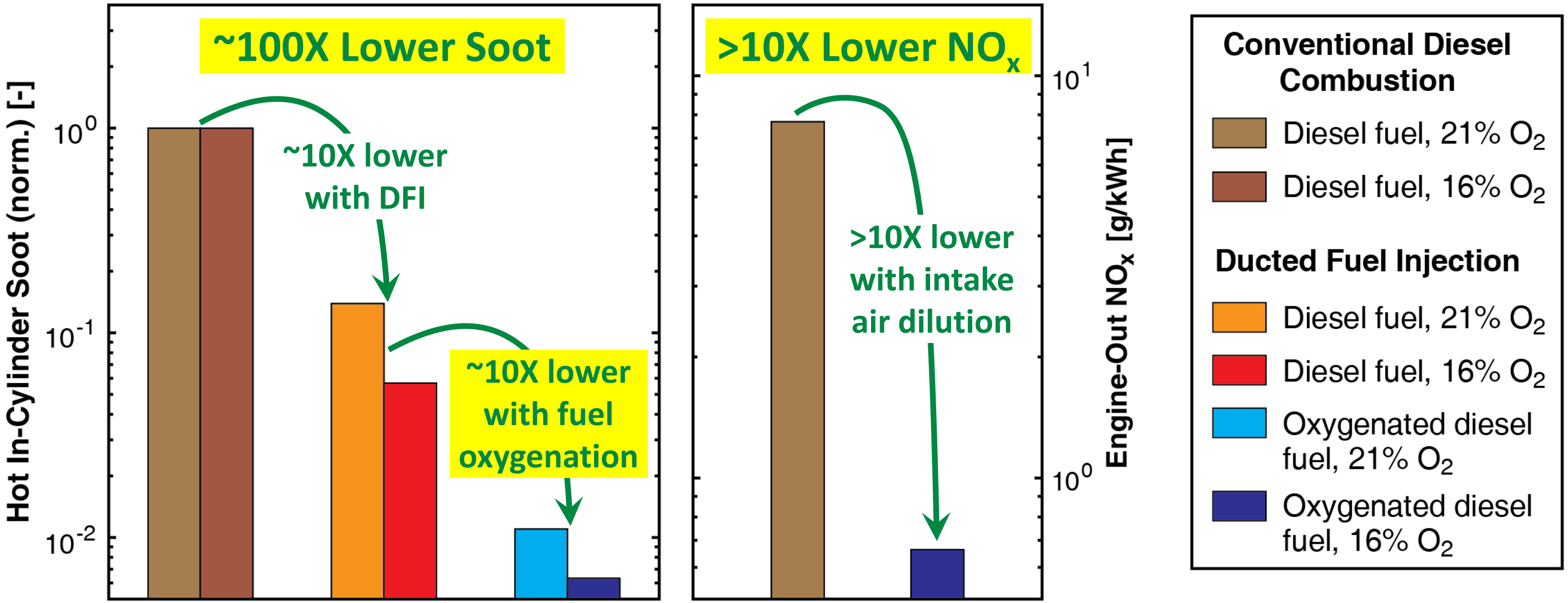
- **What is DFI?**
  - A simple, mechanical way to improve diesel combustion
  - Motivated by the Bunsen burner concept
  - Effective at curtailing (or even eliminating) in-cylinder soot
  - Tolerant to dilution, breaking the soot/NO_x trade-off





S. Ashley, https://www.scientificamerican.com/article/can-diesel-finally-come-clean/

DFI is synergistic with low-carbon, oxygenated fuels.



*Results for ~2.6 bar gross indicated mean effective pressure, 1200 rpm, steady state, 2-hole injector

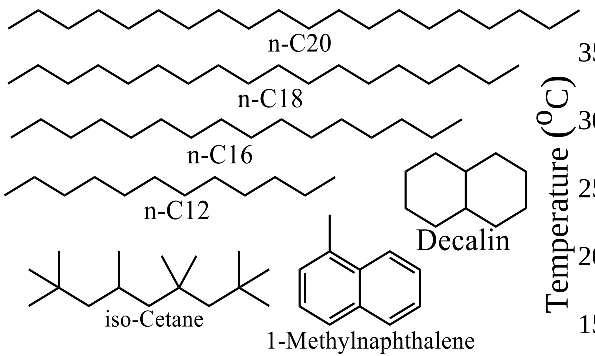
- **Additional emissions benefits from using low-carbon, oxygenated fuels with DFI provide a market incentive for their widespread use.**

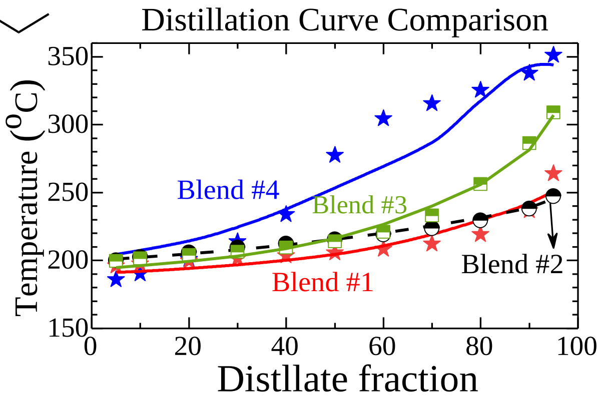
Surrogate fuel models match properties of diesel fuels and reduced kinetic mechanisms reliably predict ignition delays

Surrogate formulations

Approach: Utilize LLNL's automated surrogate optimizer to match:
- Cetane rating
- H/C ratio
- Distillation curve

Result: surrogate formulations with matched properties of a range of diesel fuels

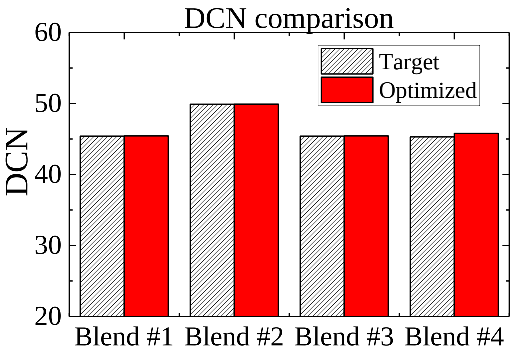


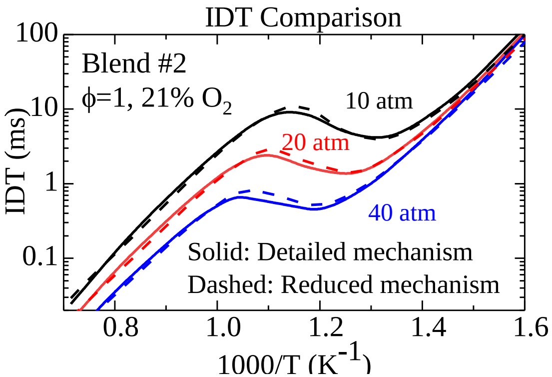


Manually reduced surrogate mechanisms

Approach: Reaction flux analysis based mechanism reduction

Result: 325 species mechanism to model oxidation, PAH formation, NOX formation and effect of NOX on ignition





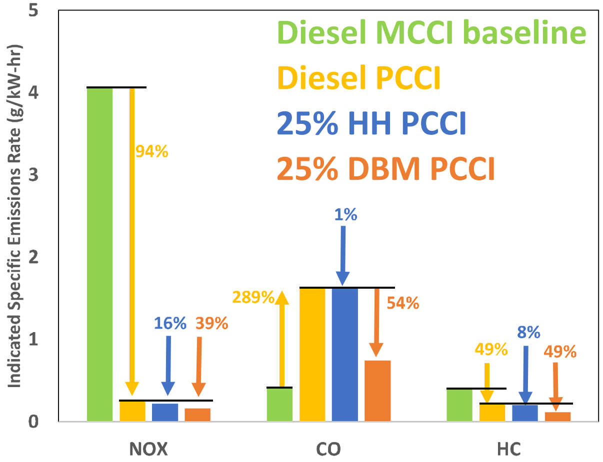
Detailed mechanism: 6500 species

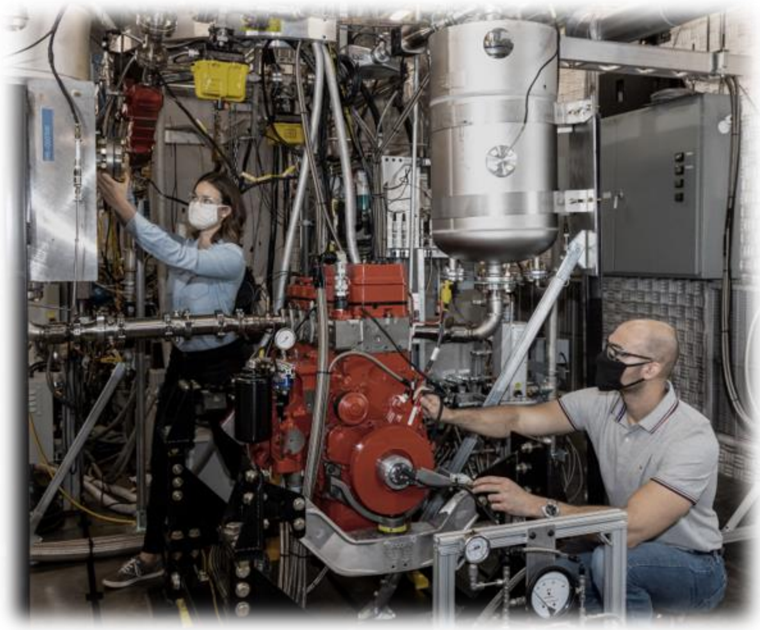
Reduced mechanism: 325 species

Lawrence Livermore National Laboratory

Oxygenated fuels reduce NO_X and HC emissions with low-load ACI when conventional exhaust is too cold for urea-SCR

- **Approach:** develop ACI (late PCCI) operation for low loads when $T_{EXH} \leq 250°C$ to reduce NOx emissions
- **Results**
  - ACI reduces NOx and HCs but increases CO
  - Bio-blends with ACI reduce NOx and HC; can mitigate CO penalty
- **Oxygenated bio-blendstocks combined with ACI may help achieve compliance with ultra-low NOx standards**



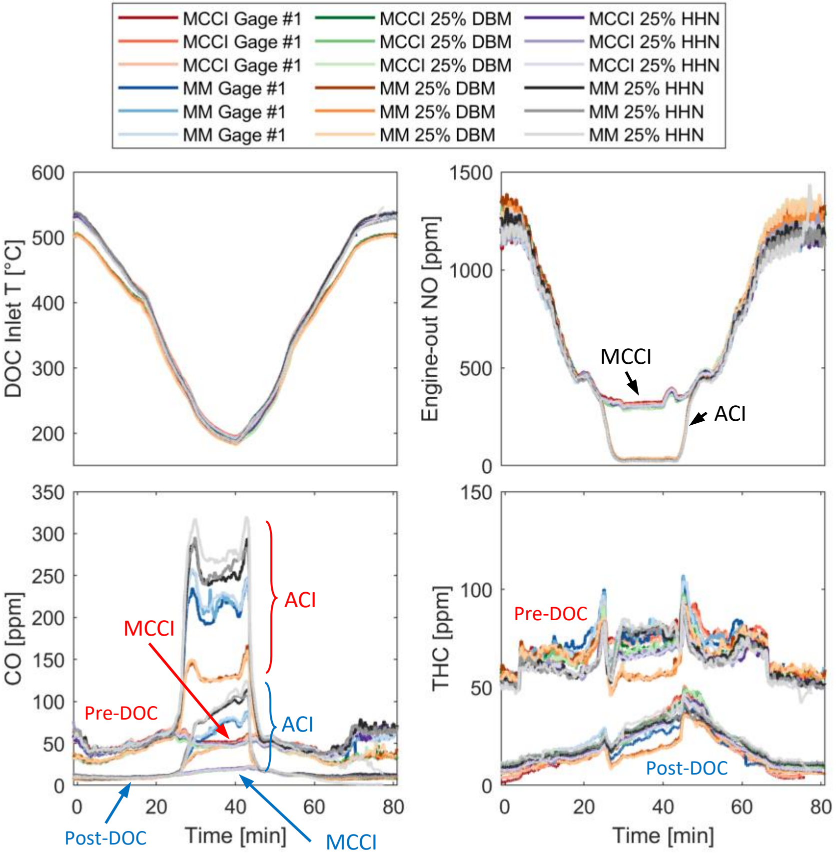


ORNL's Cummins ISB 6.7-liter-based medium-duty diesel engine converted to single cylinder operation with OEM piston and fuel injector.

OAK RIDGE National Laboratory

Mode switching and oxygenates can mitigate low-load NOx without penalties in catalyst performance

- **Approach:** Single-cylinder engine experiments; dynamic catalyst light-off/light-down characterization with MCCI vs. MCCI-ACI mode switching
- **Results:**
  - Exhaust temperatures can be maintained with a mode switching strategy
  - Mode switching and oxygenate use results only in a CO penalty
- **Mode-switching strategies may be a promising approach to reducing low-load NOx emissions during transients when exhaust temperatures drop below 250°C**



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FY21: ongoing engine combustion and emissions work

- **MCCI / cold start**
  - Mid-IR extinction technique for time-resolved detection of aldehydes in the exhaust runner: effects of oxygenate, cetane rating, and distillation properties during catalyst heating operation
- **DFI**
  - Effects of alkoxyalkanoate blend level and base diesel fuel type (i.e., from high-temperature liquefaction vs. petroleum) on DFI performance and emissions at idle and moderate-load conditions
- **ACI / multimode**
  - Cetane rating / fuel volatility impacts on multimode combustion including catalyst performance
  - CFD-based co-optimization of fuel properties and multiple injection strategies to promote ACI with lower EGR requirements

Remaining challenges for engine combustion and emissions research

- **Develop science-based guidance for fuel properties that:**
  - Reduce fuel consumption and criteria pollutant emissions
  - Enhance cold start / catalyst heating operation
  - Promote ACI combustion
- **Chemical kinetic models for bio-blendstocks to support simulation efforts**
- **Quantify impacts of GHG-neutral / GHG-negative fuels on combustion and emissions**
  - Continued collaboration with fuel properties and ASSERT teams to identify attractive candidates
  - Effects on current and future medium- and heavy-duty combustion systems
- **Continued development of DFI concept for clean, efficient, sustainable powertrains**
  - Research consortium in development

Summary

- **Co-Optima research has produced a detailed characterization of many bio-blendstocks and identified multiple attractive candidates:**
  - At least 60% lower GHG emissions than fossil diesel
  - Most can be economically produced at scale and meet fuel property targets
  - Barriers to market entry can be mitigated in many cases

- **Bio-blendstocks have beneficial effects on combustion and emissions**
  - Cleaner and potentially more efficient in conventional diesel engines, with calibration adjustments
  - Synergistic with DFI for extremely low NOx and soot emissions in mixing-controlled combustion systems
  - Can promote low-load, low-NOx ACI operation with a penalty only in CO emissions
  - Multimode MCCI / ACI strategies may help achieve compliance with ultra-low NOx emissions regulations

- **Co-Optima engine combustion researchers are well positioned to respond to the challenges of zero net-carbon fuels**

Acknowledgements

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Thank you for your attention

Questions?